

Spray-Dry Agglomerated Nanoparticles in Ordinary Portland Cement Matrix

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Abstract

Nano-sized particles have got a focus of great interest for the past decade. These ultrafine particles can have an effect in multiple ways on concrete technology. Although most of the effects of nano-particles are desired, a huge surface area introduced by nanoparticles also incorporates negative effects, such as loss of workability and safety aspects. Agglomeration of nano-sized particles by spray-drying is one potential method to overcome the negative effects. In this study, ultra-fine material was dispersed and agglomerated successfully. Agglomerate structure was analyzed and performance was evaluated with mortar samples. Agglomerated nano-sized material had micron-sized inner porosity, which enabled water penetration into the agglomerates. In water exposure, agglomerates did not dissolve although some of binder glue and dispersing agent leaked out. Water penetration and organic material leaking enabled high reactivity and workability of the agglomerated nanoparticles. In spite of the high reactivity of agglomerated nanoparticles, slightly lower final compression strengths were observed with agglomerated ultrafine particles. The results of this study can be used in concrete technology when further developing admixture technologies and recipe designs. The negative side-effects of the agglomerated nanoparticles can be overcome and accounted for within application areas.

Keywords

Concrete, Nanoparticles, Spray-Drying

1. Introduction

Nano-sized particles have been a focus of great interest for the last decades [1] [2]. Ultrafine particles, usually under a hundred nanometer a diameter, have unique qualities that larger particles of the same materials do not possess. Little by little, nanoparticles have found their way to various applications and the concrete industry is

no exception [3] [4]. In concrete, these ultrafine particles can have an effect in multiple ways. First they can act as structural components with a reinforcing effect. A good example of this type of behaviour is carbon nanotubes [5] [6]. A second set of mechanisms is the effects with their surface. An example of this type of behaviour is depollution by ultrafine titania [7] [8] and modified hydration kinetics by ultrafine calcium carbonate [9]. High surface area also increases reactivity of nanosilica [10]. Depollution effect of ultrafine titania is based on nitrogen oxide reduction by UV-light and surface catalytic properties of titania [11]. Ultrafine calcium carbonate affects cement hydration through its high surface area, offering additional nucleation sites for calcium-silicate-hydrate to precipitate [12]. Also effects of magnetic nanoparticles in concrete have been studied [13].

Although most of the effects of nanoparticles are desired, a huge surface area introduced by nanoparticles also incorporates negative effects. A loss of workability is one property that can hinder the usage of nanoparticles in the concrete industry [14]. A traditional method to overcome this type of problem is to introduce more plasticizing agent. In some cases, this is sufficient to overcome the negative effects, but the detrimental problem of simplifying the nanoparticle usage is not overcome. Also the possible hazardous nature of airborne nanosized particles is still intact [15]. Another way to overcome the problem is to manipulate the composition where the nanoparticles are introduced to concrete. An optimal composition would be a structure, where nanoparticles could maintain their reactivity with a minimal effect on concrete workability, and overcome the hazardous nature of nanosized particles.

In various other industrial applications, powders are processed with a spray-drying method [16]. In the spraydrying method, fine material is agglomerated to larger particles. Depending on the process parameters, shape, size, size distribution and qualities of the agglomerates can be modified. In this study, the goal was to manufacture nanoparticle agglomerates to be utilized in concrete technology with intact reactivity, using the spray-drying method. The spray-drying process was optimized to produce a stable structure through which water could penetrate, enabling reactivity of inner parts of the agglomerate.

Evaluation of the usability of the agglomerates was done in low water/cement-ratio mortars. As there were a number of different possibilities about how these agglomerates could affect the mixes, the mechanisms behind the agglomerates were studied using a viscometer, laser diffraction and UV/VIS-spectroscopy. The structure of the agglomerates was studied with surface acoustic infrared spectroscopy and scanning electron microscopy.

2. Materials

Ultrafine precipitated calcium carbonate (PCC, surface area 17 - 29 m^2/g) was chosen for the spray-drying agglomeration. PCC (type Calofort U) was purchased from Specialty Minerals. Two dispersants were tested: Glenium 51 was purchased from BASF (used normally as superplasticizer for concrete) and Dispex N40 from Ciba Specialty Chemicals. Polyvinyl acetate-binder glue (PVA) for the spray-drying process were from Celanese. Starch based binders, Raibond 15 and Raibond 04221 were from Raisio Chemicals. In the mortar samples, the cement used was CEM I 52.5R and aggregates were standard sand according to EN-196.

3. Methods

3.1. Spray-Drying

PCC agglomerates were manufactured using a spray-drying method. In the spray-drying process, water-based slurry containing fine solid particles and a polymeric binder was introduced into a hot cylinder chamber through a special spray atomisation nozzle. In the hot chamber the moisture was evaporated and spherical agglomerates were formed. Before the actual agglomeration process, there was a pre-stage involving slurry preparation. Careful dispersion of raw materials is a necessity for ensuring the functionality of the agglomeration in the specific application. The slurries were manufactured with a bead mill, which has been proven to be an effective tool for dispersing nano-powders (Hosokawa Alpine, Agitated Lab Ball Mill 90 AHM). Nano-sized material was processed in the bead mill with a dispersing agent until optimal dispersion was achieved. Optimal dispersion was achieved when a gradation measured with laser diffraction did not change. The amount and type of dispersion agent and type of organic binder was varied. Small sample batches for IR-, UV/VIS-, rheology- and dissolution-studies were manufactured with a laboratory scale B-290 spray dryer and larger volumes for mortar samples were manufactured using pilot scale Niro's equipment. Manufactured agglomerates and compositions are listed in Table 1.

Label	Material	Dispersing agent (w/w)	Binder (w/w)					
PCC Agglomerates 1	PCC	1% Glenium 51	2% PVA					
PCC Agglomerates 2	PCC	2% Glenium 51	2% PVA					
PCC Agglomerates 3	PCC	3% Glenium 51	2% PVA					
PCC Agglomerates 4	PCC	3% Dispex N40	2% PVA					
PCC Agglomerates 5	PCC	2% Glenium 51	2% Raibond 15					
PCC Agglomerates 6	PCC	2% Glenium 51	2% Raibond 04221					

 Table 1. Precipitated calcium carbonate agglomerates with spray-drying material compositions.

3.2. Agglomeration and Agglomerate Structure

The structure of the produced agglomerates was studied with a scanning electron microscope (JEOL-JSM636OVL) and surface acoustic infrared spectroscopy (Biorad FTS 6000, helium purged MTEC300 detector). Scanning electron microscope analyses were made from pristine agglomerates and impregnated thin sections. The particle size distributions of the slurries and the powders were determined by laser diffractometer (Lecotrac LT100) using water as a dispersant in the measurements. The mechanical strength of the powders was tested with an axial die pressing test (MTS 810). Surface acoustic infrared spectroscopy was made with various scanning frequencies, in order to have characteristic signals from various penetration depths. The peak ratio between calcite and polymer (dispersion agent + binder glue) was calculated with various penetration depths. For this purpose, characteristic peaks were indentified as 2511 cm^{-1} and 1794 cm^{-1} for calcite and 1738 cm^{-1} for polymers (dispersion agent + binder glue).

3.3. Agglomerate Dissolution

Dissolution of agglomerates was studied in pure water and saturated calcium hydroxide solutions. The agglomerate concentration was 1% (w/w) in the measurements. The agglomerates were stirred with a magnetic stirrer for a time as presented in **Table 2**. The particle distribution was measured by laser diffractometer. Similarly, mixed samples were centrifuged and decanted for UV/VIS-analysis (Hitachi U-2000 Spectrophotometer). The dry material content of the centrifuged liquid phase was determined by drying at 105°C for 24 hours. In samples for UV/VIS-analysis, a few drops of diluted salt acid were added, in order to dissolve the particles and get a measure content of dispersion agent and binder glue. The same treatment was also repeated for reference samples. The characteristic peaks, after salt acid treatment, were Glenium 51: 280 nm and PVA: 255 nm. Absorption coefficients for Glenium 51 were 280 nm: 0.103 ($R^2 = 0.99$) and 255 nm: 0.189 ($R^2 = 0.98$). For PVA, absorption coefficients were 280 nm: 0.764 ($R^2 = 1.00$) and 255 nm: 0.395 ($R^2 = 0.98$). The concentration of dissolved polymers was calculated from UV/VIS-spectra with a standard procedure to differentiate the two component system that have overlapping absorption peaks [17].

3.4. Rheological Characterization

The rheological behaviour of the agglomerates was studied with Rheotest RN 4.1 coaxial cylinder viscometer. A certain amount of the initial dry material was replaced by agglomerated particles as presented in Table 3. The resulting yield stress and plastic viscosity of the slurries were calculated according to the Bingham model.

3.5. Mortar Samples

A set of low water/cement-ratio mortars was prepared. Ultra-fine precipitated calcium carbonate was selected for the reference material, due to its ability to accelerate hydration. This quality was also chosen as the reference quality, and the effect of agglomeration of PCC was studied. Mortar samples were produced according to **Table 4**. Mortars were mixed with a Hobart 5-litre mixer with 5 minute mixing time. Halfway through mixing, the mixing bowl was scraped manually to ensure homogeneity of the prepared samples. Haegermann flow was determined according to DIN1060, immediately after mixing. Hydration was followed using semi-adiabatic calorimeter according to a method described in literature [18]. Three prisms (40 mm \times 40 mm \times 160 mm) were cast

 Table 2. Laser diffraction results from dissolution studies. Agglomerates were exposed to saturated calcium hydroxide for a given time period. Re-dispersion was not observed in pure water or saturated calcium hydroxide solution.

PCC Agglomerates 3 —	Exposure time						
	0 min	60 min	120 min	360 min	1200 min		
Passing d90 (µm)	13.7%	13.7%	14.0%	13.5%	11.8%		
Passing d50 (µm)	6.1%	6.4%	6.4%	6.1%	5.3%		
Passing d10 (µm)	1.4%	1.6%	1.6%	1.4%	1.1%		

 Table 3. Rheological studies of PCC/agglomerate-slurries. Substitution ratio of PCC with agglomerates varied from 0% - 15%. Yield stress and plastic viscosity was calculated according Bingham model.

Yield stress/Plastic viscosity -	Substitution ratio							
	0%	2.5%	5%	10%	15%			
PCC Reference	377 Pa/0.026 Pas	-/-	-/-	-/-	-/-			
PCC Agglomerates 2	-/-	227 Pa/0.0110 Pas	58 Pa/0.0124 Pas	51 Pa/0.0125 Pas	10 Pa/0.0088 Pas			
PCC Agglomerates 5	-/-	237 Pa/0.0126 Pas	201 Pa/0.0102 Pas	151 Pa/0.0108 Pas	112 Pa/0.0130 Pas			
PCC Agglomerates 6	-/-	219 Pa/0.0130 Pas	190 Pa/0.0111 Pas	120 Pa/0.0122 Pas	80 Pa/0.0125 Pas			

Table 4. Recipes and results from studied mortars.

Sample	Mix design*			Haegermann	Compression strength (MPa)			Agglomerate		
	Ag/c	w/c	a/c	sp/c	flow	t (dormant) —	1 d	7 d	28 d	strength
Ref	0.00	0.35	2.30	0.01	150 mm	8.20 h	45.1	73.6	83.0	-
Ref cem	0.00	0.33	2.14	0.01	125 mm	8.90 h	49.4	82.3	88.8	-
Ref cem II	0.00	0.30	0.30	0.01	115 mm	8.50 h	54.3	85.2	92.0	-
Ref PCC	0.05	0.35	2.25	0.01	160 mm	7.00 h	53.0	79.3	88.7	-
PCC Ag. 3	0.05	0.35	2.25	0.00	150 mm	5.80 h	42.7	60.6	88.6	0.68 MPa
PCC Ag. 4	0.05	0.35	2.25	0.00	105 mm	4.90 h	47.1	66.7	76.4	1.16 MPa
PCC Ag. 1	0.05	0.35	2.25	0.00	120 mm	5.50 h	47.9	66.2	75.4	0.64 MPa

*Ag/c = Agglomerates/cement; w/c = water/cement; a/c = aggregates/cement;sp/c = superplasicizer/cement.

for each testing age, 1 d, 7 d and 28 d. The prisms were stored at RH 100% for the first day. During ages 1 d - 28 d, the samples were stored underwater until the testing age. Compression strength experiments were done according to EN196-1.

4. Results

4.1. Agglomerate Structure

Scanning electron microscope (SEM) analysis revealed that the spray-drying method produced highly rounded particles with smooth surfaces (**Figure 1**). The size distribution of the agglomerates varied between 1 μ m - 60 μ m, having the largest peak at 20 μ m (**Figure 2**). Undispersed and dispersed samples had peaks around 1 μ m and 0.1 μ m, respectively. From impregnated thin sections, it was found that agglomerates had a micron sized inner porosity (**Figure 1**). No significant difference between the inner core and surface could be observed. The uppermost surface layer of the agglomerates was analysed using surface acoustic infrared spectroscopy. Infrared



Figure 1. Scanning electron microscopy images of pristine PCC agglomerates 3 and impregnated + polished section of PCC agglomerates 3.



Figure 2. Particle size of undispersed ultrafine calcium carbonate, dispersed ultrafine calcium carbonate and ultrafine calcium carbonate agglomerated with spray-drying method. Agglomerated particles had diameter $\sim 20 \mu m$, whereas undispersed had mean diameter $\sim 1 \mu m$ and dispersed $\sim 0.1 \mu m$.

spectroscopy signals from the PCC and the organic binder were compared with various penetration depths (**Table 5**). It was found that the organic material/PCC-signal ratio was relatively constant at various penetration depths. The changes in signal ratios were comparable to PCC/PCC-ratio changes which indicated that changes were within the limit of divergence. IR-analysis concluded that the polymers and initial material were evenly distributed throughout the whole surface layer to bulk layer.

4.2. Agglomerate Dissolution and Rheology

Table 2 presents results from the dissolution studies in saturated calcium hydroxide and pure water solutions. Degradation of agglomerates did not happen during measurements as can be seen from laser diffraction studies in **Table 2**. Exposure to water or saturated calcium hydroxide solution did not significantly dissolve the agglomerates. A small amount of dissolution happened. The content of dissolved material was determined with UV/VIS-spectroscopy. The centrifuged phase of dissolution samples was dim and dissolution of particles with salt acid was necessary in order to perform UV/VIS-measurement. It was observed that notable dissolved Glenium was 0.026 g/g and PVA 0.024 g/g for PCC agglomerates 2. The amount of dissolved Glenium was 0.055 g/g and PVA 0.026 g/g for PCC agglomerates 3. These amounts were compared to the total dry material concentration

Table 5. Results of infrared spectroscopy study. Scanning frequencies and signal ratios for polymers and PCC. (PCC = Precipitated Calcium Carbonate, Polymers = Glenium 51, PVA). Various scanning frequencies correspond to various penetration depths, 40 kHz absorbed on top layers and 2.5 kHz penetrated deepest into sample.

PCC Agglomerates 4 –	Scanning frequency						
	40 kHz	20 kHz	10 kHz	5 kHz	2.5 kHz		
PCC/PCC-ratio (2511 cm ⁻¹ /1794 cm ⁻¹)	1.003	1.002	0.978	0.934	0.944		
Polymers/PCC-ratio $(1738 \text{ cm}^{-1}/2511 \text{ cm}^{-1})$	0.083	0.064	0.087	0.081	0.080		



Figure 3. Composition of pristine PCC agglomerates and detached material in water solution. Agglomerate content of the studies slurry was 1%. Majority of the leached materials was binder glue or dispersing agent.

and the difference was assumed to present detached PCC-content. It was concluded that the organic material dissolved significantly more than pure decomposition of agglomerates would produce.

4.3. Performance Characterization

A small replacement of the initial nano-material with agglomerates, produced a huge reduction in the initial yield stresses of the PCC slurries (**Table 3**). This phenomenon was also observed in mortar-samples. PVA/Glenium-combination had largest plasticizing effect. Further evaluation revealed that the plasticizing effect can be mainly explained with superplasticizer leakage from the agglomerated particles, but the effects of the highly rounded particles could not be ruled out.

Results from mortar experiments are listed in **Table 4**. Addition of PCC shortened the dormant period and agglomerated PCC particles had the same effect. The Haegermann flow of studied mortars varied between 100 mm - 160 mm. Compression strengths of mortars containing agglomerates were slightly lower than reference mortars. Agglomerate strength did not a have correlation to mortar prisms' compression strengths.

5. Discussion

The spray-drying method proved to be an effective technique to agglomerate nanoparticles to a desired composition. The agglomerated particles were a composite of nanoparticles, dispersing agent and binder glue. According to SEM observations, these agglomerated nanoparticles were highly rounded with micron-sized inner porosity. The composition between the surface and inner core did not differ. Laser measurements revealed that no significant dissolution of agglomerates happened in aqueous- or saturated calcium hydroxide solutions. In rheology measurements, a huge plasticizing effect was observed when small portion of initial nanoparticles were replaced with agglomerated particles. The leakage of binder glue and dispersing agent was found to be the main reason for the plasticizing effect. The leakage of polymers from agglomerated particles enabled water to penetrate into the agglomerated particles. The penetrated water made it possible for the inner surfaces of agglomerates to react, which can explain the high reactivity of agglomerated nanoparticles.

In order to estimate benefits gained by agglomeration, a set of mortars was studied. The reference quality, hydration acceleration, was judged against the flowing ability of the mortars. The reference samples had a dormant period approximately 8 - 9 hours. Addition of ultra-fine precipitated calcium carbonate lowered the dormant period to 7 hours. Addition of agglomerated particles produced mortars with dormant period of 5 - 6 hours. With agglomerated particles, it was also seen that the leaked superplasticizer lengthened the dormant period, but the effect was smaller compared to mortars with PCC and superplasticizer.

The negative effects of this agglomeration method were observed in compression strengths. The compression strengths were lower with agglomerate-samples compared to the reference samples. The precipitated calcium carbonate/superplasticizer-combination enhanced compression strengths in 1d results, slowly lowering over time to the reference level. Agglomerate-samples had lower compression strengths from day one and the effect was emphasized with time. Agglomerated particles probably caused microstructural defects to the samples, therefore lowering the compression strengths which were largely dependent on the quality of the microstructure [19]-[21]. Agglomerate strength did not have any correlation to the mortar sample compression strengths. It is also likely that other qualities which are largely depended on microstructure could also be affected, e.g. durability.

6. Conclusion

The spray-drying method was effective at agglomerating ultra-fine particles used in concrete technology. Agglomeration improved workability of mortars with nanosized particles, while still maintaining the high reactivity of nanoparticles. The high reactivity originated from the beneficial water penetration to the agglomerates, which was mainly caused by leaking of organic material from the agglomerates. These qualities made it possible to produce highly-reactive and -flowable mortar. Agglomeration method provided easy method to overcome dusting effect of pristine ultra-fine particles. Another method to overcome dusting is to use nanoparticles as slurries. However, slurries will introduce additional water, increasing transportation volumes and complicating mix design. With agglomerated particles can ease handling of nanoparticles, if the safety issues prove to be relevant. Agglomeration was observed to have a negative effect to mortars microstructure, causing lowering of compression strengths. The results of this study can be used in concrete technology when further developing admixture technologies and recipe designs. The negative side-effects of the agglomerated nanoparticles can be overcome and accounted for within application areas.

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